

**DEACTIVATION (NEUTRALIZATION OR DETOXIFICATION) AND
SAFE DISPOSAL OF GERMICIDES AND PESTICIDES****Organized by****P. Zhu**

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Boston, MA August 18-22, 2002

**REMEDIATION OF FUMIGANT COMPOUNDS IN THE ROOT ZONE
BY SUBSURFACE APPLICATION OF AMMONIUM THIOSULFATE**

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Introduction

Fumigants are widely used to control soil-borne pests, such as nematodes, fungi, and weeds, in soils to be planted to high-cash-value crops. Fumigant compounds have high vapor pressures and thus exist in soils largely in the gas phase and a significant proportion of the applied mass is volatilized from the soil surface. Because fumigant compounds have broad toxicity and are highly mobile, application methods emphasize containment to prevent air and water contamination by these compounds. Containment also maximizes efficacy by increasing the time for which high fumigant concentrations are present in the soil. Management practices to reduce emissions include tarping the soil surface with impermeable plastic, sealing the soil surface with water to reduce diffusion at the soil surface, and applying fumigants via subsurface drip irrigation to reduce gas-phase diffusion. Another promising approach to reducing emissions involves enhancing fumigant degradation at the soil surface. Previous research has indicated that nucleophilic compounds such as ammonium thiosulfate (ATS) rapidly transform and detoxify halogenated fumigants such as methyl bromide, propargyl bromide, and 1,3-dichloropropene^{1,2}. Application of ATS at the soil surface can significantly reduce emissions of halogenated fumigants^{3,4}. Addition of nucleophilic compounds has no impact on non-halogenated fumigants such as methyl isothiocyanate (MITC).

Emissions-reduction strategies are required to minimize air contamination by fumigants and to increase efficacy. However, retention of significant concentrations of fumigants in soil following the fumigation period may result in groundwater contamination through leaching, continued volatilization to the atmosphere, and phytotoxicity to the crop planted following fumigation. In some current soil fumigation practices using 1,3-dichloropropene (1,3-D), the fumigant is applied with water through subsurface drip irrigation lines. Similar application methods have been proposed for potential alternative fumigants such as propargyl bromide (PrBr). In these experiments, we investigated the potential for subsurface application of ATS to reduce soil concentrations of 1,3-D and PrBr following soil fumigation, thus reducing the threat of groundwater contamination and potential phytotoxic effects on the crop.

Methods

Four concrete mesocosms (3 m long x 1.5 m wide x 1.6 m deep) were filled with washed river sand to a bulk density of 1.4 Mg m^{-3} . Beds were formed at the soil surface; dimensions are indicated in Figure 1. Subsurface drip lines (HDPE) were installed 15 cm below the bed surface. Fumigants were mixed with 24 L of water in HDPE carboys, which were then connected to the drip lines and pressurized to apply the fumigant mixture to the mesocosms. Application required 2-3 hours. Fumigant application rates were typical of field application: 10 gal ac^{-1} of 1,3-D C-35; 80 lb ac^{-1} of PrBr; and 17 gal ac^{-1} of Vapam (MITC precursor). These application rates corresponded to 0.2 to 0.3 mol of 1,3-D, PrBr, and MITC added to each mesocosm. After a 10-day fumigation period, ATS was drip-applied to half of the mesocosms in the same manner (380 mL of Thio-Sul fertilizer in 24 L water, $\sim 2 \text{ mol}$ of ATS). The remaining two mesocosms received 24 L of water (no ATS) to indicate fumigant concentrations remaining in the root zone with no ATS treatment.

Soil gas samples were collected to determine fumigant concentrations remaining in the soil. Teflon tubing (1-mm ID) was buried during bed construction and tubes terminated from 20 to 80 cm below the soil surface throughout the bed cross-sectional area (locations indicated in Figure 1) to provide information on the distribution of fumigant compounds in the root zone. Gas samples (50 mL) were collected on activated charcoal adsorbent tubes; syringes were used to apply vacuum and to measure the gas volume sampled. Fumigant compounds were extracted from charcoal using 3 mL of acetone. Fumigants were identified and quantified by gas chromatography, using ECD for PrBr and 1,3-D and NPD for MITC. Soil gas concentrations of fumigants were measured just prior to ATS application, and were monitored for 7 days following ATS application. Concentration data were kriged to construct contour maps of soil gas concentrations throughout the soil profile. The volume contained under the contours was determined to indicate the mass of fumigant remaining in the monitored zone of each mesocosm.

Results

Soil gas samples collected prior to ATS application indicated that significant concentrations of halogenated fumigants remained in the root zone following a 10-day

fumigation period. Soil concentrations increased with increasing containment, so that the highest post-fumigation concentrations were observed in the plots covered with impermeable plastic and the lowest concentrations were observed in untarped mesocosms. These soil concentrations ranged over an order of magnitude, and indicated the potential for highly effective containment to result in high post-fumigation concentrations in the root zone.

Fumigant concentrations in the root zone were depleted more rapidly in ATS-treated mesocosms than in mesocosms receiving only water (Figures 1 and 2). Concentrations presented in Figure 1 were normalized to the concentrations measured just prior to ATS application to account for differences in the initial PrBr concentration. At 52 hours after ATS addition, the total PrBr in the monitored zone (indicated by the volume under the contours) was ~20% of the PrBr present prior to ATS application (Figure 1A). In the mesocosm receiving no ATS, the PrBr remaining at 52 hours was ~60% of the initial PrBr (Figure 1B). Similar results were observed for 1,3-D isomers.

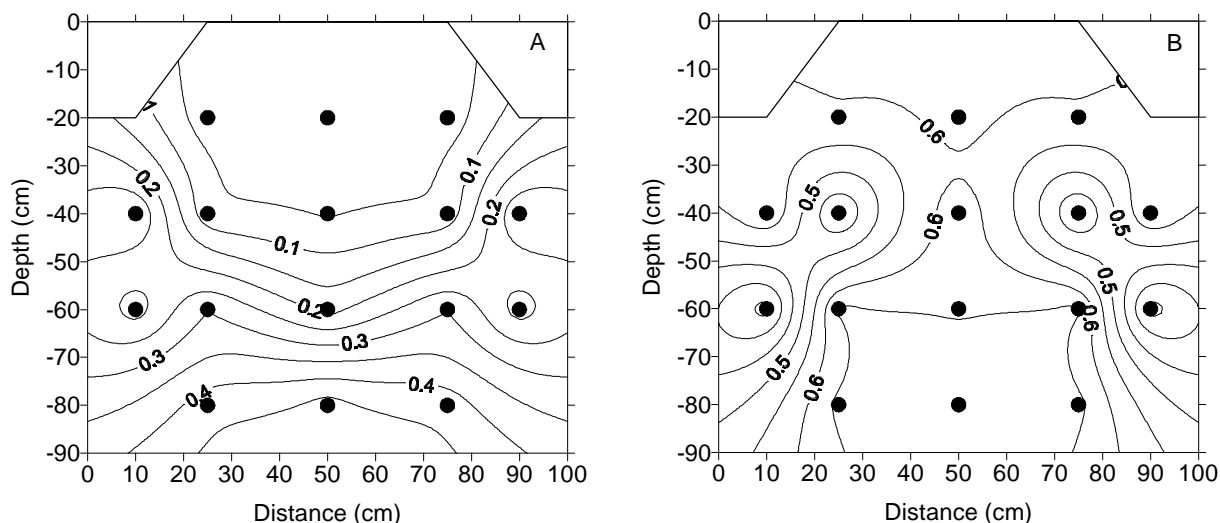


Figure 1. Soil gas concentrations for propargyl bromide in (A) a mesocosm receiving ATS and (B) a mesocosm receiving water only (no ATS) at 52 hours after ATS/water addition. Points indicate the location of soil gas samples. The concentration at each point was normalized to the concentration measured at that location just prior to ATS/water application. Contours were constructed by kriging the data.

Non-linear regression to a first-order dissipation model ($C = C_0 e^{-kt}$) indicated that the decay constant (k , h^{-1}) for halogenated fumigants was ~5 times greater in ATS-treated than non-treated mesocosms (Figure 2A). Because MITC is not affected by ATS application (no chemical reaction occurs between MITC and ATS), MITC was dissipated in ATS-treated and non-treated mesocosms at approximately the same rate (Figure 2B). Results were consistent over an order-of-magnitude range in initial fumigant concentrations, as indicated by the error bars in Figure 2.

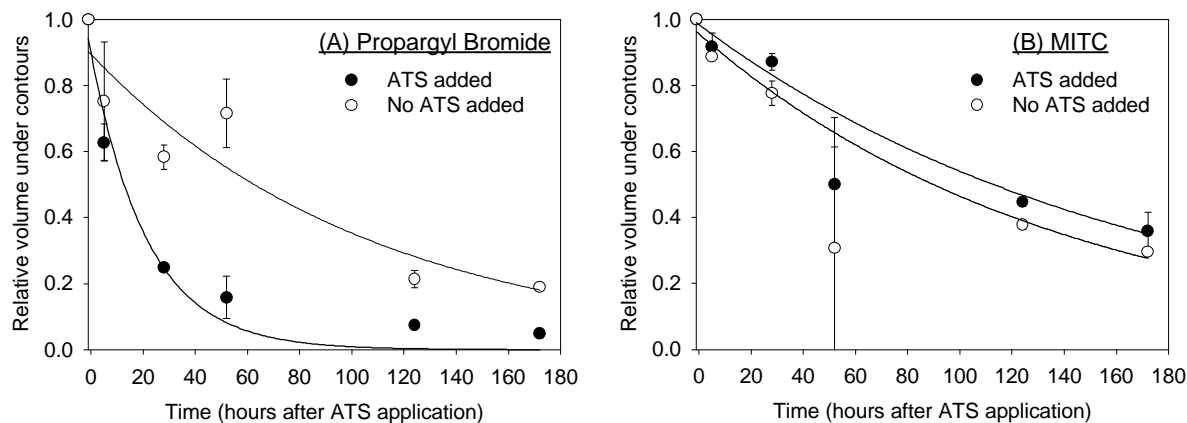


Figure 2. Decrease in fumigant concentration in the root zone with time. Values indicate the total volume contained under the concentration contours; the volume at each time was normalized to the volume observed just prior to injection of ATS/water. Values are the mean of two mesocosms and error bars represent the standard error. Lines indicate regression to a first-order kinetic model. For MITC (B), regression omitted spurious 52-hour data.

These results indicate that for situations in which residual concentrations of halogenated chemicals are present in the soil, subsurface application of nucleophilic compounds such as ATS may be valuable for reducing the threat of leaching, runoff, and phytotoxicity to crops. This approach may be particularly useful for remediation of chemicals applied via drip irrigation, including soil fumigants and other pesticides, since the application of ATS through existing drip lines would result in a minimal additional expense. Thiosulfate compounds, including ammonium, potassium, and calcium thiosulfate, are commonly-used fertilizers and pose little toxicity threat. Since ATS has been shown to degrade other halogenated agrichemicals, such as some chlorinated acetanilide herbicides, this approach has promise for root-zone remediation of many soil-applied chemicals.

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